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Investigations of Porosity Enhanced Removal of Fuel Containing Carbon Codeposits by Thermo-Chemical Removal

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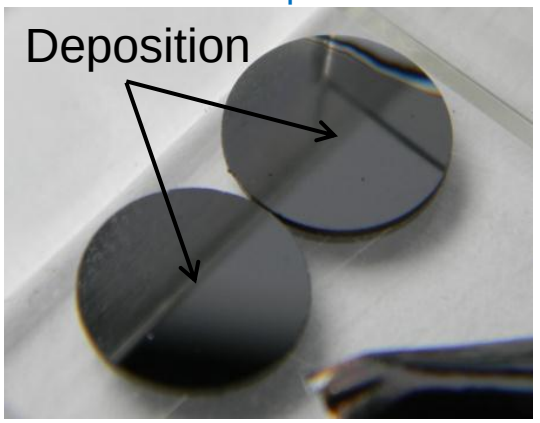
Fuel Retention in Fusion Devices

- Carbon based wall materials release carbon (C) due to the contact with the hydrogen plasmas in fusion devices

  → amorphous hydrogenated carbon layers (a-C:H) are formed on reactor surfaces

  - *Tritium-Codeposition (T)*
  - *Fuel retention and safety problems (e.g. ITER)*

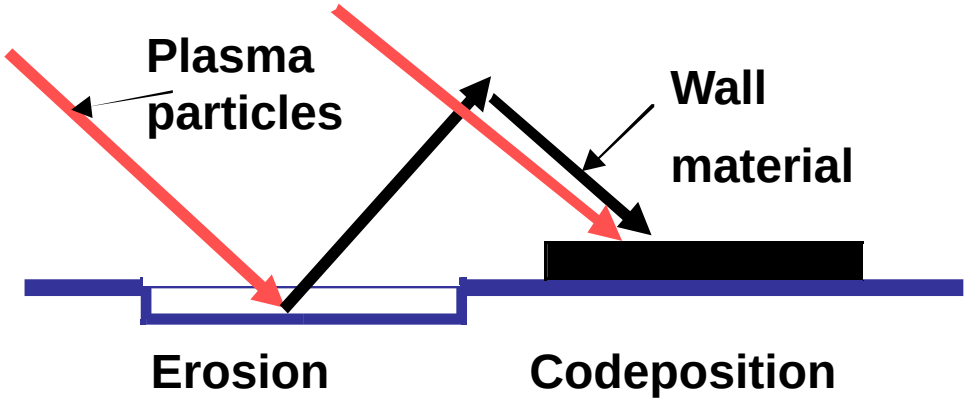
a-C:H on Si deposition in Lab

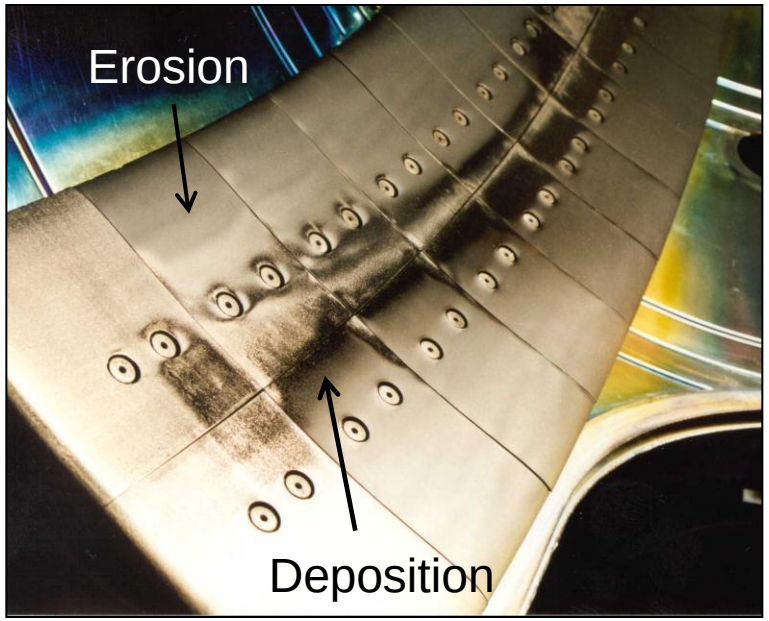


Deposition in Tokamak

→ Removal of codeposits necessary

Development of codeposits





Option: Thermo-Chemical Erosion (TCE)

- **Treatment of codeposits with heat and chemical reactants**
  - Very homogenous and B-Field compatible
  - Needs high wall temperatures (>300°C for O_2) and pressures (>5mbar) to be effective
  - Most effective with O_2 or NO_2, then known as oxygen baking
  - Removal of Carbon and fuel isotopes (H,D,T) is partially decoupled
  - Lack of in-depth theory describing the process, so far

Typical reactions

$2C + O_2 \rightarrow 2CO$

$C + O_2 \rightarrow CO_2$

$2H_2 + O_2 \rightarrow 2H_2O$

- **Goals of this study**
  - Develop a theory for the process
  - Compare it with available data (mainly from Davis, Univ. of Toronto)
  - Derive suggestions for maximum removal rate in fusion devices

Porosity Enhanced Removal

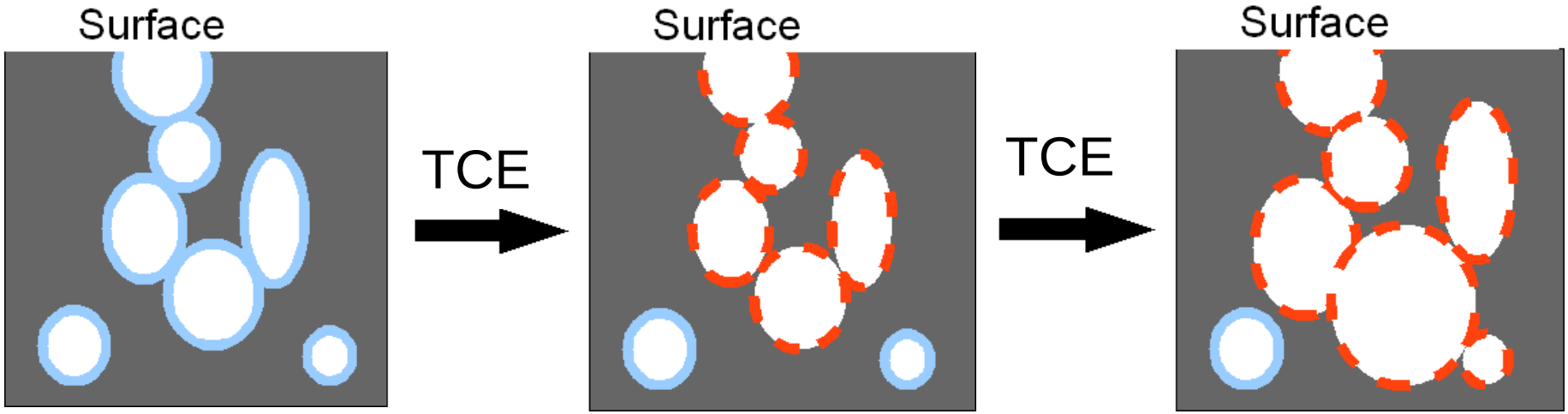
Initially nanopores form ~10% of the layer volume

Open pores form a network which is accessible from the surface

Pore surface area, H/C and mass density of layers are connected

By Thermo-Chemical Erosion:

- The pore walls adsorb removal gas
- *Pore sizes and thus the porosity increase*
- *Thickness reduces only slowly*



Analytical Removal equation

The general description can be derived from differential reaction-diffusion equation

$$Dn''(x) - kn(x) = 0$$

Only for layers >>25µm or T_S ~1000K the diffusion limits reaction rate, otherwise diffusion is fast enough to be neglected

Homogenous 2nd order chemical reaction equation in the **reaction limited** regime of removal rate of atoms per area and time:

R

Thickness of layer

Number of reacting removal gas particles

$$R = \int_0^z k(T_S) \times n_{Gas}(x) \times n_{D,C}(x)\, dx \xrightarrow{reaction\ limited} R = k\, n_{Gas} n_{D,C} \int_0^z dx \Rightarrow$$

Chemical reaction rate (Arrhenius)

Pore volume per area

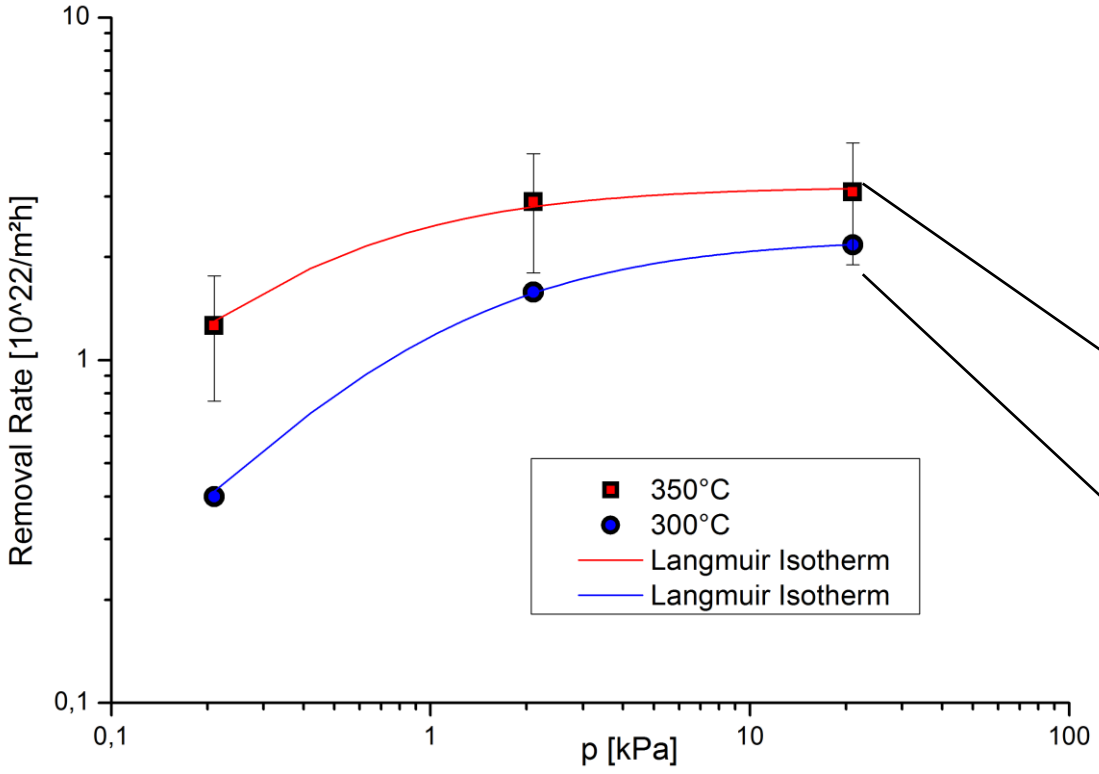
$$R(T_S, p_{Gas}, z) = P * \sqrt{\frac{\pi k_B T_S}{2 m_{Molecule}}} * e^{-\frac{E_A}{k_B T_S}} \times \frac{z * C_{Por}}{V_{Molecule}} * \frac{K_L p_{Gas}}{1 + K_L p_{Gas}} \times n_{D,C}$$

Maximum particles per area

Langmuir adsorption of particles in pores

Comparison with available experimental data

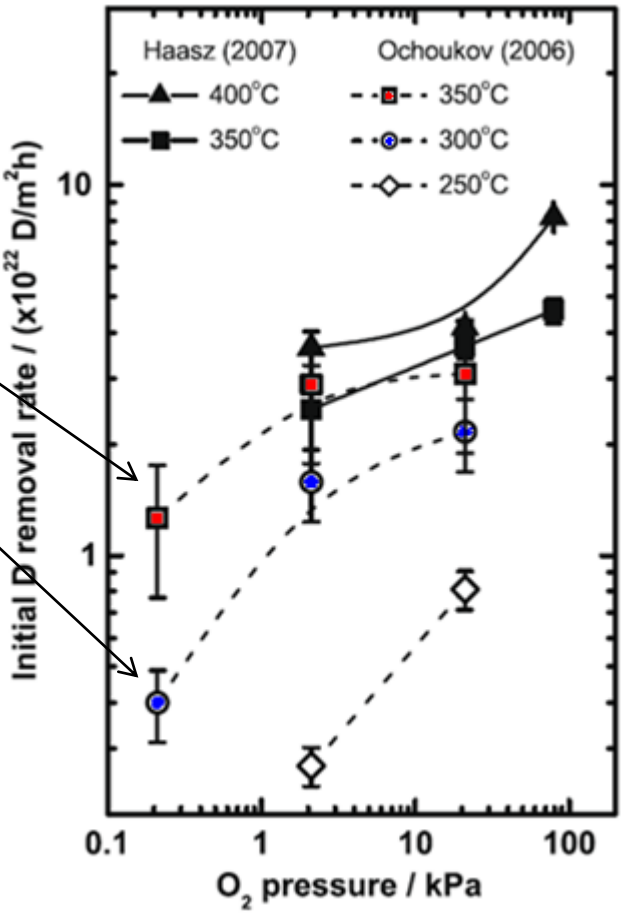
Pressure Dependence



Fit is in agreement with data

$$R = C(T_S, z) * \frac{K_L p_{gas}}{1 + K_L p_{gas}}$$

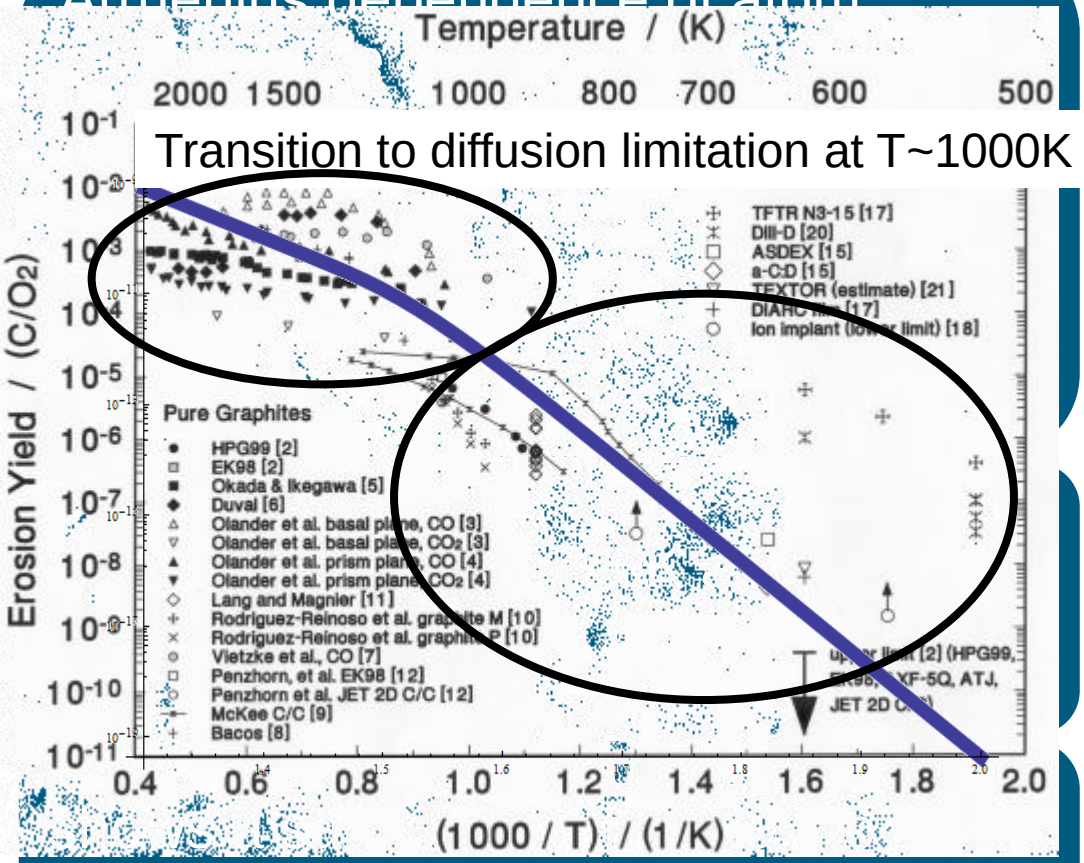
Pressure dependence of the atom removal rate



[Davis, JNM 390-391 (2009), 532-537]

Temperature Dependence

Arrhenius dependence of atom

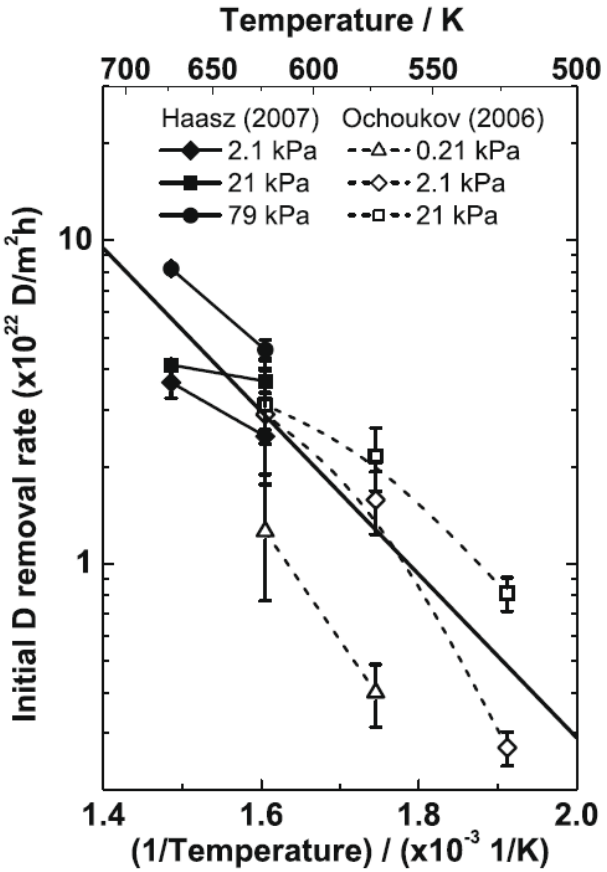


transition from a reaction limited to a diffusion limited process at high temperatures

$$R = C(z, p_{Gas}) * \sqrt{\frac{\pi k_B T_S}{2 m_{Molecule}}} * e^{\frac{E_A}{k_B T_S}}$$

[Davis, Phys. Scr. 91 (2000), 33-35]

Temperature dependence of the atom removal rate



[Davis, JNM 390-391 (2009), 532-537]

Thickness Dependence

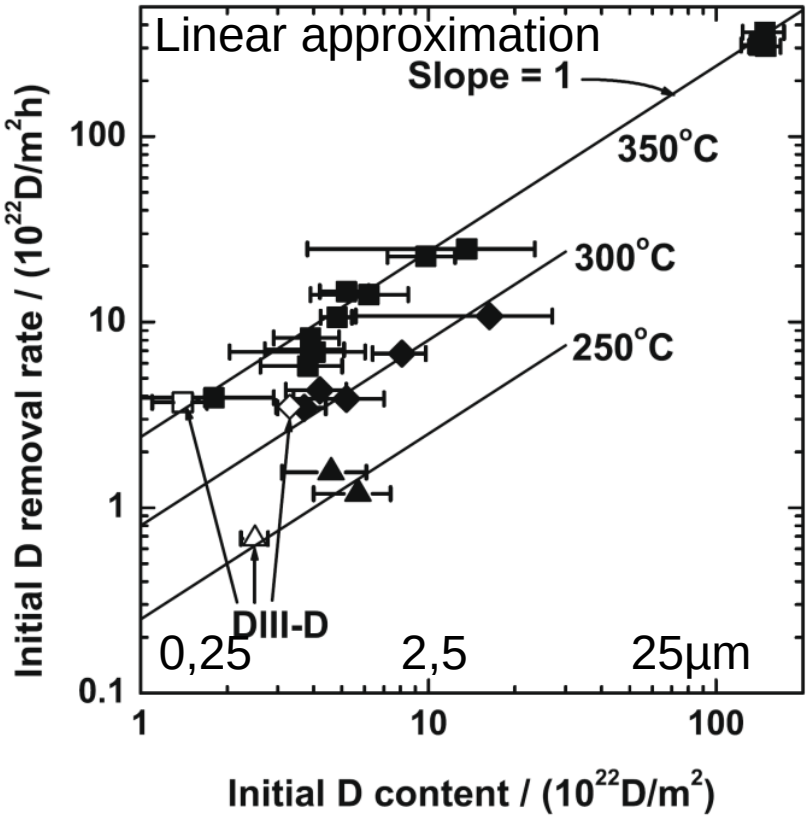
A linear dependence of the removal rate on the initial atom content (which is proportional to the layer thickness) is seen in a study by Davis

The model shows a linear dependence with thickness z

$$R = C(T_S, p_{Gas}) * z$$

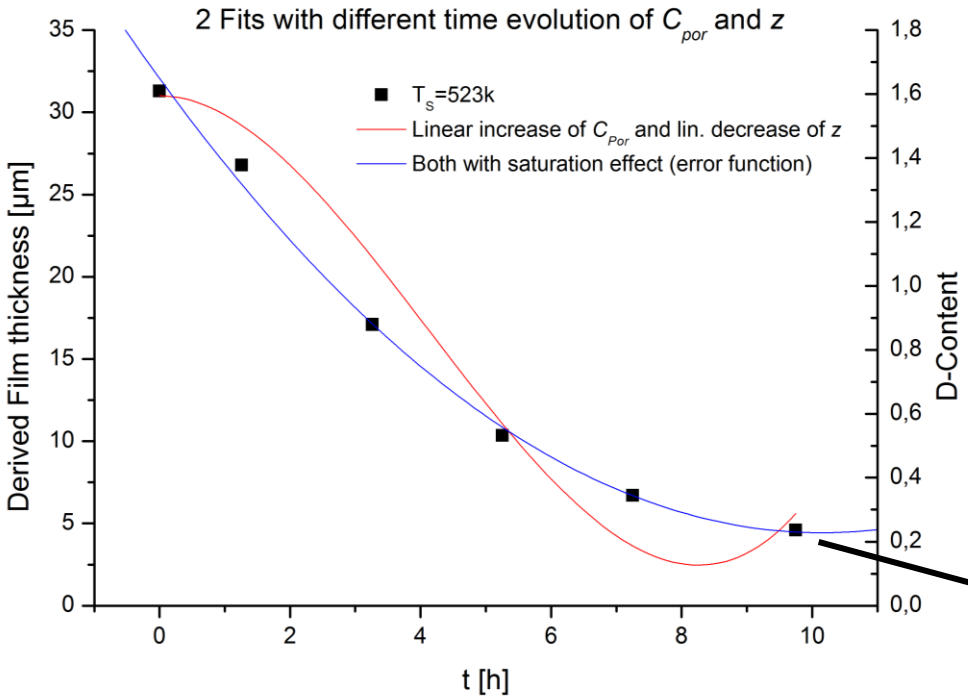
A diffusion limitation does not appear at thicknesses <25µm, when considering Davis‘ results

Effect of the initial areal atom density, i.e. thickness, on the removal rate

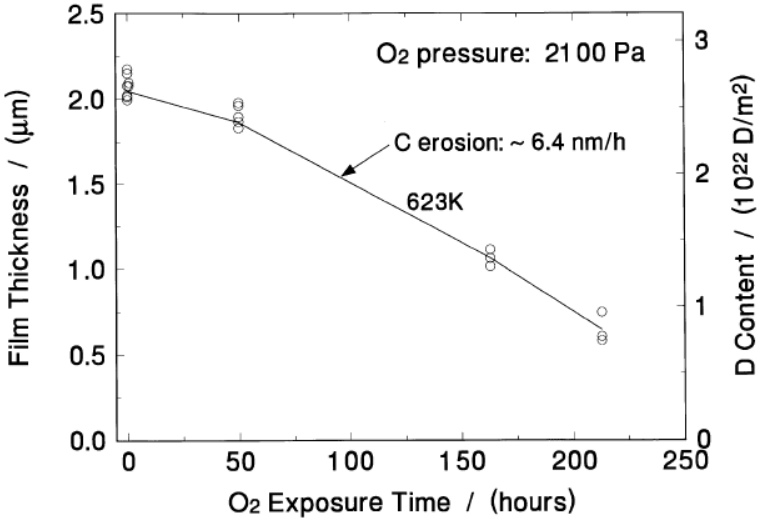


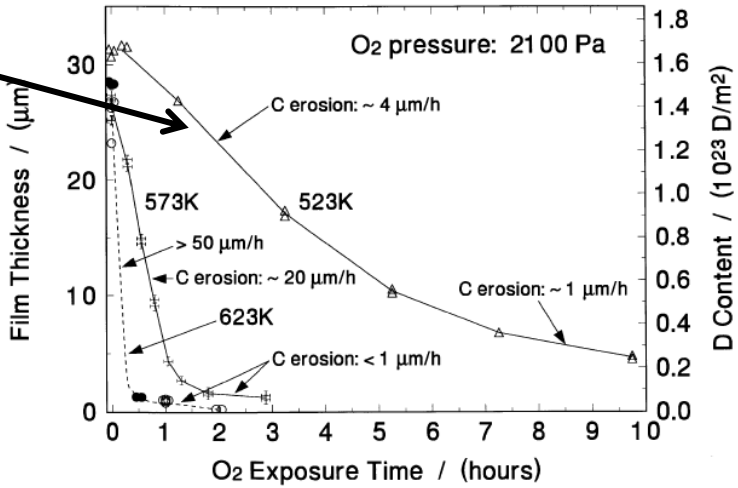
[Davis, JNM 390-391 (2009), 532-537]

Time Dependence



Time evolution of the layer D content





$$R = C(T_S, p_{Gas}) * z(t) * C_{Por}(t)$$

$$R = C(T_S, p_{Gas}) * z(t) * C_{Por}(t)$$

This behaviour is in contrast to the constant removal rate of plasma based methods

[Haasz, Davis, JNM 256 (1998), 65-68]

Conclusions for fuel retention handling

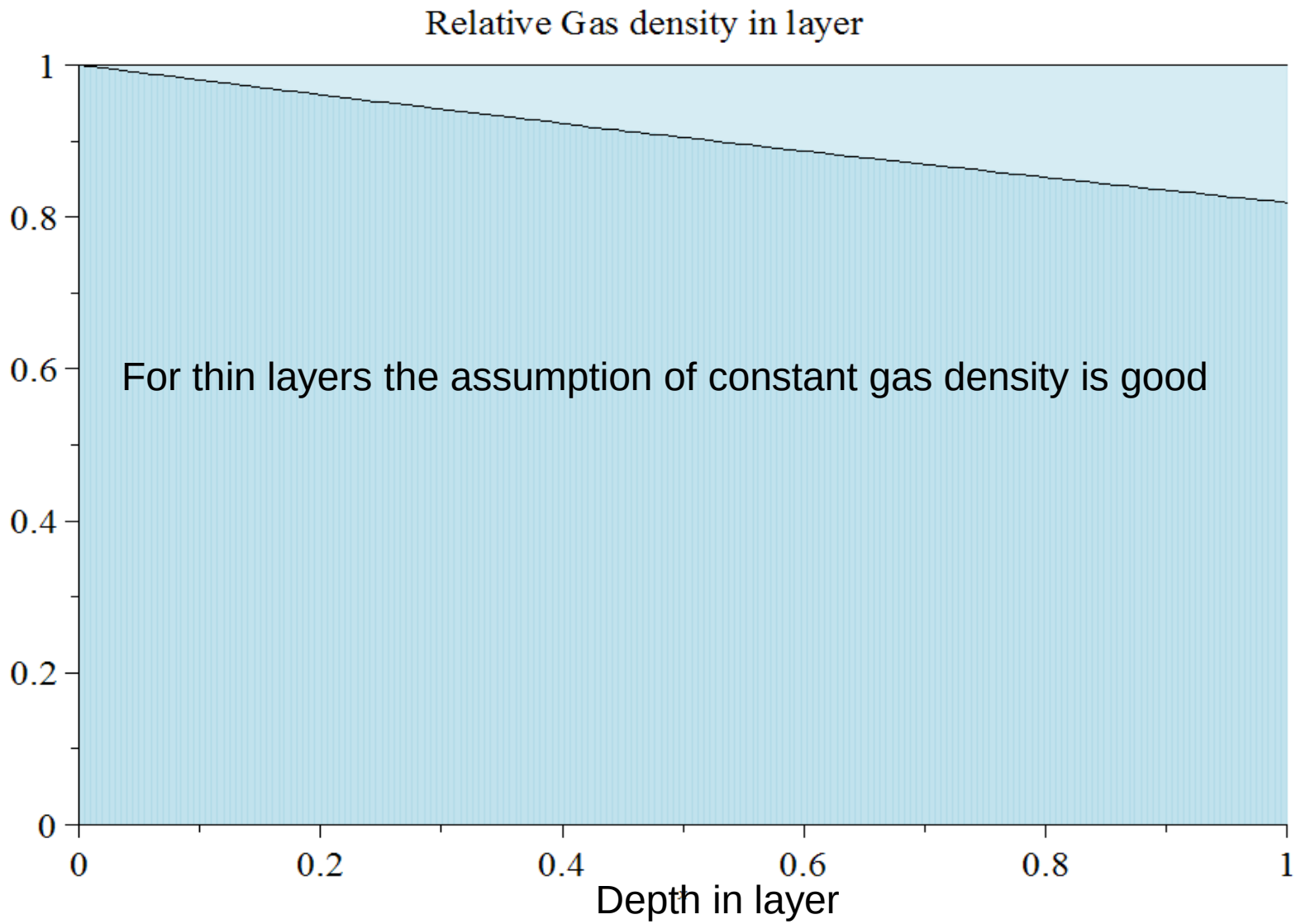
- A physical, analytical model describing the removal process has been developed
- Removal rate increase with both temperature and pressure

  → *use highest possible values for Thermo-Chemical removal, but yield decreases with p_{Gas}>20mbar, T_S>700K*
- Removal rate is mostly proportional to layer thickness

  → *Thermo-Chemical removal should be applied on a medium-term basis (e.g. 10 ITER discharges), with plasma cleaning of retained oxygen and layer remainders afterwards*
- A combination of thermo-chemical removal with plasma removal can be the fastest removal method, when switching at the right time

  → *A modelling software including the derived formulas and parameters is planned, in order to predict removal rates and times for future devices*

Gas balance in the layer



For thin layers the assumption of constant gas density is good

Solving the Reaction-Diffusion Equation

$$Dn''(x) - kn(x) = 0$$

1-D differential equation for the concentration of the removal gas *n* in dependence of the depth *x* at steady state

- Diffusion coefficient D, Arrhenius-type reaction coefficient k

$$n(0) = C_{Por} \times \frac{K_L p_{Gas}}{1 + K_L p_{Gas}}$$
$$n(\infty) = 0$$

Boundary conditions

- At the layer surface (x=0) gas concentration is determined by the outer gas density and relative volume porosity C_{por}
- A saturation with pressure is described by Langmuir Adsorption with coefficient K_L
- At infinite thickness no gas is left over

$$n(x) = \left(C_{Por} \times \frac{p_{Gas}}{k_B T}\right) \times e^{-x\sqrt{k/D}}$$

Solution *n(x)* shows an exponential concentration decrease with depth *x* of layer

General Removal equation

The total amount of gas in the layer *N* is the integral of *n* over the layer thickness *z*

$$N(z) = \int_0^z n(x)dx = \sqrt{\frac{D}{k}}(1 - e^{-z\sqrt{\frac{k}{D}}})(C_{Por} \times \frac{K_L p_{Gas}}{1 + K_L p_{Gas}})]$$

Total removal rate *R* is given by amount of removal gas N times the probability of a reaction per time *k*

$$\boldsymbol{R = k(T_S) \times N(z, C_{Por}) \times N_{D,C} \Rightarrow}$$

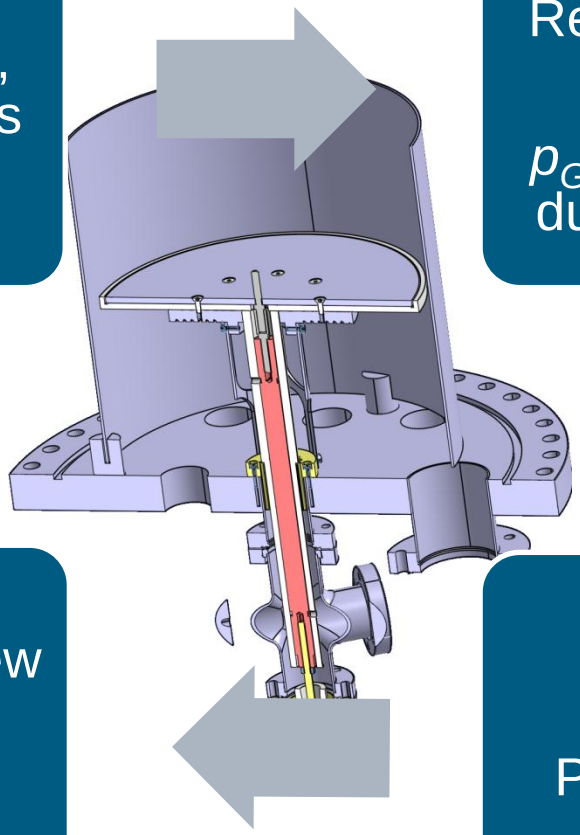
$$\boldsymbol{R = P\, e^{-\frac{E_A}{T_S k_B}} \times \sqrt{\frac{D}{k}}\left(1 - e^{-z\sqrt{\frac{k}{D}}}\right)\left[C_{Por} \times \frac{K_L p_{Gas}}{1 + K_L p_{Gas}}\right] \times N_{D,C}}$$

In total 5 free parameters remain, which have to be determined experimentally

- Temperature dependence: P, E_A
- Porosity dependendent values: C_{Por}, K_L, D

Experimental test of the thickness dependence

Laboratory carbon layers on Si for constant and known layer properties, but different thicknesses (5 steps from 200-3200nm)



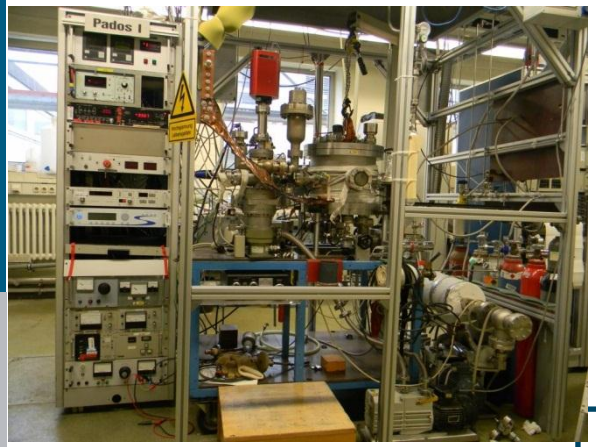
Thermo-Chemical Removal with oxygen at T_S=350°C and p_{Gas}=10mbar with same durations t for all layers

Removal rate determination by Ellipsometry, Profilometry, µg-scale with pre/post measurements

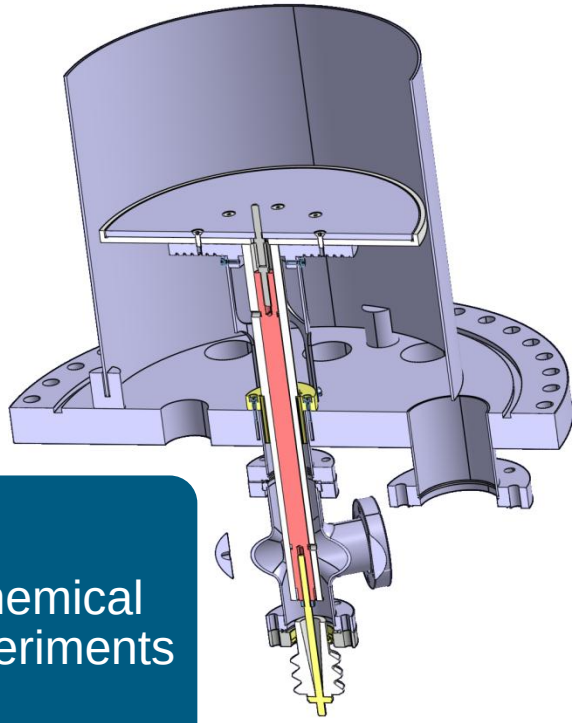
Fitting of model to the new experimental data and comparison with other experiments

Experimental device PADOS

Photo of PADOS



CAD image of new internal structure



Vacuum device PADOS has 2 distinct configurations

RF-Glow Discharge Plasmas for deposition and cleaning

- Measurement of T_{wall} (deposition parameter)
- High deposition rates (1µm/h)
- Sheath potentials down to ~100V for layer density control
- Thick layers (>several µm)

Thermo-Chemical removal experiments

- Capillary tube for <1bar gas analysis by QMS
- T_{wall} = 25…700°C
- Toxic and explosive gases
- Little background deposits

Sample Preparation

Polished Silicon Substrates

- Low surface roughness
- Good adhesion of a-C:H also for thick layers
- Large area >40cm² samples available
- Advantages for NRA, QMS, Ellipsometry, Profilometry, µg-scale

All Layers have similar Properties

- Deposition in similar condition RF-discharges in CD_4 in PADOS
  - All free parameters, except *z (thickness)*, are similar for all layers
- 5 different layer thicknesses by 5 different deposition durations

Layer Property Determination

- Ellipsometry and Profilometry for thickness measurement
- Areal Carbon density by µg-scale and thickness
- NRA measurements planned for D determination

Removal Experiments

Thermo-Chemical removal in Oxygen

- 10mbar, T_{wall} = 350°C
- Same conditions for all layer thicknesses

Mass spectrometry

- Determination of exhaust products
- Safety aspects of oxygen cleaning
- Assessment of thickness effects

Fitting of Model to Data

- Test of model with new data
- Comparison with other oxygen experiments at similar conditions (e.g. Davis, my Diploma thesis)